

## Coating composition and tetrahydroxy oligomer precursor therefor.

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### Abstract

A novel tetrahydroxy oligomer crosslinkable with amine-aldehyde resins to form a coating composition adapted for use as an automotove topcoat and which upon curing forms a hard, glossy, coating with outstanding durability and excellent resistance to solvents and water. The coating composition comprises: (A) a tetrahydroxy oligomer having a number average ( $M_n$ ) molecular weight of between about 600-2000 and being the reaction product of: (i) an ester containing pendant hydroxyl and carboxyl functionality and being made by reacting: (a) a C3-C10 aliphatic diol, and (b) an alkyl hexahydrophthalic anhydride, wherein (a) and (b) are combined in the reaction mixture in an amount sufficient to allow reaction in about a 1 : 1 molar ratio; and (ii) a diepoxyde having a number average molecular weight between about 130-1500, wherein (i) and (ii) are combined in the reaction mixture in an amount sufficient to allow reaction in about a 2:1 molar ratio, (B) an amine aldehyde or polyisocyanate crosslinking agent; and (C) optionally a hydroxyl functional additive.

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㉞ Coating composition and tetrahydroxy oligomer precursor therefor.

㉟ A novel tetrahydroxy oligomer crosslinkable with amine-aldehyde resins to form a coating composition adapted for use as an automobile topcoat and which upon curing forms a hard, glossy, coating with outstanding durability and excellent resistance to solvents and water. The coating composition comprises:

(A) a tetrahydroxy oligomer having a number average ( $\bar{M}_n$ ) molecular weight of between about 600–2000 and being the reaction product of:

(i) an ester containing pendant hydroxyl and carboxyl functionality and being made by reacting:

(a) a C<sub>3</sub>–C<sub>10</sub> aliphatic diol, and

(b) an alkyl hexahydrophthalic anhydride, wherein (a) and (b) are combined in the reaction mixture in an amount sufficient to allow reaction in about a 1:1 molar ratio; and

(ii) a diepoxyde having a number average molecular weight between about 130–1500, wherein (i) and (ii) are combined in the reaction mixture in an amount sufficient to allow reaction in about a 2:1 molar ratio,

(B) an amine aldehyde or polyisocyanate crosslinking agent; and

(C) optionally a hydroxyl functional additive.

**A1**

**EP 0 088 193**

- 2 -

DESCRIPTION

COATING COMPOSITION AND TETRAHYDROXY  
OLIGOMER PRECURSORS THEREFOR

1 This invention relates to coating compositions and tetrahydroxy oligomer precursors therefor.

Because of increasingly strict solvent emissions regulations in recent years, low solvent emission paints have become very 5 desirable. A number of high solids paint compositions have been proposed to meet these low solvent emission requirements. However, many of these compositions are deficient because of difficulty in application, slow curing rates, lack of flexibility, poor durability and low solvent and water resistance.

10 According to the present invention, there is provided a coating composition which preferably contains at least 60% by weight, more preferably greater than 70% by weight, of nonvolatile solids, and which comprises:

(A) a tetrahydroxy oligomer having a number average ( $\bar{M}_n$ ) molecular weight of from 600 to 2000 and being the reaction product of:

(i) an ester containing pendant hydroxyl and carboxyl functionality and being made by reacting:

(a) a C<sub>3</sub> - C<sub>10</sub> aliphatic branched diol and  
(b) an alkyl hexahydrophthalic anhydride ,

20 wherein (a) and (b) are combined in the reaction mixture in an amount sufficient to allow reaction in about a 1:1 molar ratio; and

(ii) a diepoxide having a number average molecular weight of from 130 to 1500,

25 wherein (i) and (ii) are combined in the reaction mixture in an amount sufficient to allow reaction in about a 2:1 molar ratio;

(B) a crosslinking agent;

(C) 0-50 weight percent based on the total weight of (A), (B),

30 (G) and (D) of a hydroxy functional additive having a number average molecular weight ( $\bar{M}_n$ ) of from 300 to 5000, preferably from 500 to 2500; and

(D) solvent.

- 3 -

1        The crosslinking agent (B) may comprise an amine-aldehyde crosslinking agent or a polyisocyanate crosslinking agent.

5        The amine-aldehyde crosslinking agent is included in the composition in an amount sufficient to provide at least 0.60, preferably from 0.75 to 3.75, equivalents of nitrogen crosslinking functionality included in the composition either on the tetrahydroxy oligomer or as a hydroxyl group of the hydroxy functional additive. The polyisocyanate crosslinking agent is included in the composition in an amount sufficient to provide  
10      from 0.5 to 1.6, preferably from 0.8 to 1.3 reactive isocyanate groups per hydroxyl groups included in the composition either on the oligomer or on the hydroxy functional additive.

15      The oligomers of this composition are compatible, in particular, with low molecular weight hydroxy functional acrylics. In addition, the high solids coating composition of this invention may include additives such as catalysts, antioxidants, UV. absorbers, flow control or wetting agents, antistatic agents, pigments, plasticizers, etc. The oligomers of this composition are also compatible with nonaqueous dispersions (NAD's), which  
20      are generally used as flow control additives.

The invention also includes the tetrahydroxy oligomer as defined at (A) above.

The preferred coating composition of this invention provide a system which is particularly suitable for those applications requiring a coating having high gloss, hardness, durability and high solvent and water resistance as well as low temperature cure.  
The desirable

- 4 -

characteristics of the coating composition of this invention, in particular the excellent physical properties and weatherability, are believed to result from the steric hinderance to hydrolysis afforded the ester groups of the 5 oligomer by the alkyl group of the anhydride. However, while this theory has been advanced, to explain the excellent durability of this coating composition, neither its validity nor its understanding is necessary for the practice of the invention.

10 Each of the components of the coating composition, the amounts of each of the components required to achieve the desired results of the invention and a method for applying the composition are described hereinafter in greater detail.

#### Tetrahydroxy Oligomer

A principal material in the coating composition of this invention is a novel tetrahydroxy oligomer having a number average molecular weight ( $\bar{M}_n$ ) between about 600 and about 2000, more preferably between about 700 and about 20 1500. The oligomer is prepared by first combining a low molecular weight C<sub>3</sub> - C<sub>10</sub> aliphatic branched diol with an alkyl hexahydrophthalic anhydride in the reaction mixture in an amount sufficient to allow reaction in about a 1:1 molar ratio to form an ester having pendant hydroxyl and 25 pendant carboxyl functionality. A slight excess of anhydride than needed for this reaction may be used. This ester is subsequently reacted with a diepoxide; the ester and the diepoxide being combined in the reaction mixture in an amount sufficient to allow reaction in about 30 a 2:1 molar ratio, forming the oligomer. By means of this reaction, the carboxyl of the ester opens the epoxide groups of the diepoxide generating two more hydroxyl functionalities.

- 5 -

The aliphatic branched diol preferably contains only one primary hydroxyl group, the second hydroxyl of the diol is therefore preferable a secondary or tertiary hydroxyl, more preferably a secondary hydroxyl.

5      Additionally it is preferable that the hydroxyl groups not be on adjacent carbons and more preferably be separated by at least three carbon atoms. The carbon chain may also be interrupted or substituted by non-interfering functionality. Suitable C<sub>3</sub> - C<sub>10</sub> aliphatic branched diols  
10     include but are not limited to, 2-ethyl-1,3-hexane diol, 1,3-butanediol and 1,2-butane-diol with 2-ethyl-1,3-hexanediol being most preferred. Other suitable diols will be apparent to one skilled in the art. Mixtures of suitable diols can also be used.

15     The alkyl hexahydrophthalic anhydride preferably contains a lower alkyl group, i.e., an akyl group having about up to seven carbons, more preferably, up to about four carbons. Additionally, the alkyl group may be substituted by non-interfering functionality. Suitable  
20     anhydrides useful in this invention include methyl hexahydrophthalic anhydride, and its ethyl and propyl analogs, with methyl hexahydrophthalic anhydride being most preferred.

25     The diepoxide suitable for use in this invention is a low molecular weight epoxy containing two epoxide groups per molecule and has a number average molecular weight of between about 130-1500. This diepoxide can be a liquid or a solid and can be either a single diepoxide or a mixture of suitable diepoxides. Examples of suitable  
30     diepoxides include but are not limited to condensation products of bisphenol-A with epichlorohydrin, examples of which are commercially available as Epon 828, 1001, 1004, 1007 and 1009 (marketed by Shell Oil Company), Araldite 6010 and 8001 (marketed by Ciba-Geigy); ester-type diepoxides  
35     such as diglycidyl phthalate, diglycidyl adipate, and diglycidyl glutarate; cycloaliphatic diepoxides such as dicyclopentadiene and vinyl cyclohexane dioxide and

- 6 -

aliphatic ether type diepoxides such as ethylene glycol, diglycidyl ether, 1,2-propylene glycol diglycidyl ether and 1,4 butanediol diglycidyl ether (Araldite RD-2 marketed by Ciba-Geigy).

5 In preparing the tetrahydroxy oligomer, the diol and anhydride are combined, generally by adding the anhydride dropwise to the heated diol, and then reacted at an elevated temperature for a time necessary to complete the esterification reaction. Subsequently, the diepoxide  
10 diepoxide is reacted with the ester composition, generally in the presence of a catalyst, and the composition is maintained at elevated temperatures until the reaction between the hydroxy acid ester and diepoxide is complete. Preferred carboxyl/epoxide catalysts useful in preparation  
15 of hydroxy functional oligomer are the tetralkyl ammonium salts such as tetra methyl ammonium chloride, tetraethyl ammonium bromide and trimethyl benzyl ammonium chloride as well as metal salts of a carboxylic acid, such as potassium octoate or chromium III octoate. Other useful catalysts  
20 include: metal halides such as chromium trichloride, ferric trichloride, and aluminum trichloride; mercaptans and thioethers such as octyl mercaptan, dimercapto propanol and dimercapto-diethyl ether; tertiary amines such as triethyl  
25 amine, pyridine, dimethylaniline, quinoline, B-picoline, ethylpyridine; and the like. Still other catalyst known to catalyze carboxy/epoxy reactions will be apparent to those skilled in this art.

Various mixtures of these types of oligomers may also be employed within the scope of the compositions of  
30 the invention described herein.

Although the above reactions may be carried out with or without solvent, it is generally suitable and preferable in order to achieve the preferred high solids

concentration of the coating composition to use little or no solvent. However, when desirable, suitable solvents which may be employed include those commonly used, such as toluene, xylene, methyl amyl ketone etc. It is however necessary to incorporate solvent into the coating composition in order to facilitate application of the coating composition. Typically solvents useful in the coating composition to facilitate application, for example spray application at high solids content, include those commonly employed, such as toluene, xylene, methyl amyl ketone, acetone, dioxane, butanone, 1-ethanol, 2-butoxyl-1-ethanol, diacetone alcohol, tetrahydrofuran, butyl acetate, cellosolve acetate, dimethyl succinate, dimethyl glutarate, dimethyl adipate or mixtures thereof. The solvent in which the tetrahydroxy functional oligomer of the coating composition may be prepared, may be employed as the solvent for the coating composition thus eliminating the need for drying the oligomer after preparation, if such is desired. As mentioned above, the nonvolatile solids content of the high solids coating composition is preferably at least 60% and more preferably 70% or more, thus limiting the amount of solvent included in the composition. However, while the tetrahydroxy oligomer of the subject composition are particularly suitable for making high solids coatings, they are also suitable in compositions that are not high solids compositions. Determination of optimal solids content (with the corresponding solvent content) for a given application would be within the skill of one in the art.

- 8 -

Crosslinking Agent

1        A second component of the paint compositions of this invention  
is a crosslinking agent which may be an amino-aldehyde or a  
polyisocyanate.

Amine-aldehyde Crosslinking Agent

5        Suitable amino-aldehyde crosslinking agents are well known  
in the art. Typically, these crosslinking materials are products  
of reactions of melamine, or urea with formaldehyde and various  
alcohols containing up to and including 4 carbon atoms. Preferably,  
the amine-aldehyde crosslinking agents useful in this invention  
are amine-aldehyde resins such as condensation products of  
10      formaldehyde with melamine, substituted melamine, urea, benzo-  
guanamine or substituted benzoguanamine. Preferred members of  
this class are methylated melamine-formaldehyde resins such as  
hexamethoxymethylmelamine. These liquid crosslinking agents have  
substantially 100 percent nonvolatile content as measured by the  
15      foil method at 45°C for 45 minutes. For the purposes of the  
preferred high solids coatings of the invention it should be  
recognised that it is important not to introduce extraneous  
diluents that would lower the final solids content of the coating.  
Other suitable amine-aldehyde crosslinking agents would be apparent  
20      to one skilled in the art.

Particularly preferred crosslinking agents are the amino  
crosslinking agents sold by American Cyanamid under the trademark  
"Cymel". In particular, Cymel 301, Cymel 303, Cymel 325 and Cymel  
1156, which are alkylated melamine-formaldehyde resins are useful  
25      in the compositions of this invention.

The crosslinking agent reactions are generally catalytically  
accelerated by acids. One such catalysts, for example, which may  
be so employed is p-toluene sulfonic acid, generally added to the  
composition in about .5% by weight based on the total weight of  
50      ester and crosslinking agent.

The amine-aldehyde materials function as a crosslinking  
agent in the composition of the invention by reacting with the  
hydroxyl functionality of the tetrahydroxy oligomer and by reaction

- 9 -

- 1 with the hydroxyl functionality on the hydroxy functional additive if such material is included in the composition.

In order to achieve the outstanding properties which make these coating compositions particularly useful as automotive top-  
5 coat materials, it is essential that the amount of amino crosslinking agent be sufficient to substantially completely crosslink the hydroxyl functionality in the coating composition. Therefore, the amino crosslinking agent should be included in the composition in an amount sufficient to provide at least about 0.67 equivalents,  
10 preferably between about 0.75 and about 3.75 equivalents, of nitrogen crosslinking functionality for each equivalent of hydroxyl functionality included in the composition either as a hydroxyl group on the optional hydroxy functional additive or on the tetrahydroxy oligomer.

Polyisocyanate Crosslinking Agent

15 The polyisocyanate crosslinking agent is a compound having 2 or more, preferably 3 or more, reactive isocyanate groups per molecule. This polyisocyanate crosslinking agent is included in the compositions of the invention in an amount sufficient to provide between about .5 and about 1.6 preferably between about .8  
20 and about 1.3, reactive isocyanate groups per hydroxyl group in the composition. Most preferably the crosslinking agent is included in an amount sufficient to provide about 1.1 isocyanate groups per hydroxyl group in the composition.

Polyisocyanates are well known in the art and numerous  
25 suitable isocyanates having 2 or more reactive isocyanate groups per molecule will be apparent to those skilled in the art. Among the many suitable polyisocyanates are aliphatic, cycloaliphatic and aromatic isocyanate compounds. Representative of the numerous isocyanates which may be employed are (1) aliphatic diisocyanates  
30 such as trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, 1,2 propylene diisocyanate, 1,2 butylene diisocyanate, 2,3 butylene diisocyanate, 1,3 butylene diisocyanate, ethylidene diisocyanate, butylidene diisocyanate, 4,4'-bis (isocyanate hexyl) methane,

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